THESIS

Subject THE COMPOSITION OF WATERS IN MINES OF SULPHIDE ORES.

Name Edwin T. Hodge.

The Composition of Waters in Mines of Sulphide Ores.

A Thesis Submitted to the Faculty of the Graduate School of the University of Minnesota

by

EDWIN T. HODGE

In partial fulfillment of the requirements for the degree of Master of Arts.

1914.

REPORT

of

COMMITTEE ON THESIS

THE undersigned, acting as a committee of the Graduate School, have read the accompanying thesis submitted by Edwin Thomas Hodge, for the degree of Master of Arts. They approve it as a thesis meeting the requirements of the Graduate School of the University of Minnesota, and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Arts.

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The Composition of Waters in Mines of Sulphide Ores.

The deposition and superficial alteration of ore deposits are doubtless complex processes and unlike many laboratory experiments the results cannot be reduced to simple chemical formulae. Generally the investigator sees only the end products of the reactions, he does not supply the material nor does he determine the conditions that obtain. Geologic theory, therefore, has been built up mainly by inference or by testing repeatedly promising working hypotheses. Some of these hypotheses have been tested so often under widely differing conditions, and have been found applicable at so many places, that they have become accepted theories, if not indeed principles of geology. Thus it is incontrovertible that some sulphide ores have been deposited by cold circulating underground waters and many have been enriched by solution and redeposition by ground waters in the superficial zone. One cannot estimate exactly the character of the waters

that are the agents of superficial alteration and enrichment, but the best available index is to be found in the waters that are now circulating through sulphide ores and that may be collected in mines exploiting deposits of these ores. Some fifty analyses of waters from sulphide ores are available. They vary greatly in concentration and for that reason the constitution of the various waters is not readily compared. To facilitate such a comparison the analyses have been reduced to percentage of total solids, and the various radicles have been expressed as molecular or reacting values and arranged in groups intended to bring out these relations most clearly.

Table I.

In table I[a], opposite page 6, the analyses are numbered consecutively.

a. 1, 2, 3, 4, 5, 6, 7, Butte, Montana. W. F. Hillebrand analyst. Weed, W. H., Geology and ore deposits of Butte District, Montana: Prof. Paper U. S. Geol. Survey No.74, 1912, p.101.

8, 9, 10, 11, 12, Capote Mine, Cananea, Mexico. G. W. Hawley, analyst. Emmons, W. H., The enrichment of sulphide ores: Bull. U. S. Geol. Survey No.529.

13, Burra Burra mine, Ducktown, Tenn., first level below black copper workings. R. C. Wells, analyst. Emmons, W. H., and Laney, F. B., Preliminary report on the mineral deposits of Ducktown, Tenn: Bull. U. S. Geol. Survey No. 470, 1911, pp. 171,172.

14, 15, Callaway shaft, Ducktown, Tenn., at water level. R. C. Wells, analyst. Emmons and Laney, Preliminary report on the mineral deposits of Ducktown, Tenn.: Bull. U. S. Geol. Survey No. 470, 1911, pp. 171-172.

16, East Tennessee mine, Ducktown, Tenn., R. C. Wells, analyst. Emmons and Laney, idem.

17, 18, Ducktown, W. H. Emmons, Sulphide enrichment, loc. cit.

19, Joplin, Mo., analyses by Buehler, H. A., and Gottschalk, V. A. Data Geochemistry, Clark, F. W.; Bull. U. S. Geol. Survey No.491.

20, Joplin, Mo. Analysis by H. N. Stokes. Data of Geochemistry, loc. cit,

21, Joplin, Mo. Data of Geochemistry, p.177. loc. cit.

22, 23, 24, 25, Rothschönberger Stolln, Freiberg, Germany. A. Frenzel, analyst. Beck, Richard, The nature of ore deposits (translated by W. H. Weed), vol.2, 1905, p.377.

26, 27, 28, Hauraki, Auckland. The Geology of the Waihi-Tairua subdivision, Bell, J. M., and Fraser, Colin: Publications of New Zealand Geological Survey No. 15.

29, Stanley mine, Idaho Springs, Colo. L. J. W. Jones, analyst. Jones, L. J. W., Ferric sulphate in mine waters and its action on metals: Proc. Colorado Sci. Soc., vol.6, 1897-1900, p. 48.

30, Mizpah mine, Tonopah, Nev., from bore hole 2,316 feet deep. R. C. Wells, analyst.

31, Savage mine,(Comstock lode), Storey County, Nev., 600-foot level.

32, 33, Gould & Currey mine (Comstock lode), Storey County, Nev.

34, Hale & Norcross tunnel section (Comstock lode), Storey County, Nev.

35, C. & C. shaft (Comstock lode), Storey County, Nev., 2,250-foot level. N. E. Wilson, analyst. Reid, J. A., The structure and genesis of the Comstock lode: Bull. Dept. Geology Univ. California, vol.4, 1906, p. 189.

36, Central tunnel (Comstock lode), Storey County, Nev., vadose water. N. E. Wilson, analyst. Reid, J. A., loc. cit., p.192.

37, 38, Ely district, Nev., Chalcocite enrichment, Spencer, Arthur C.: Econ. Geol. vol. 8, no. 7, 1913, p.621.

39, Bachelor mine, Creede, Colo. Iron includes some aluminum. Water is alkaline. Chase Palmer, analyst.

40, Solomon mine, Creede, Colo. Iron includes some aluminum. Water is alkaline. Chase Palmer, analyst.

41, 42, Homestake mine, S. Dakota. W. J. Sharwood, Econ. Geol., vol.6, 1911, p.738.

44, Federal Loan mine, Nevada City, Cal., 400-foot level. W. F. Hillebrand, analyst. Lindgren, Waldemar, The gold-quartz veins of Nevada City and Grass Valley, California: Seventeenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1896, p. 121.

45, Black Prince mine, Nevada City, Cal., 400-foot level. W. F. Hillebrand, analyst. Lindgren, idem.

46, Victoria Reef, Western Australia Mineral Deposits, Lindgren, Waldemar.

47, 48, Geyser mine, Custer County, Colo. W. F. Hillebrand, analyst. Emmons, S. F., Seventeenth Ann. Rept. U. S. Geol. Survey, pt.2, 1896, p.462.

49, 50, Sulphur Bank, California. Analyses by Melville, W. H. G. F. Becker, Mon. U. S. Geol. Survey,vol. 13, 1888, p.259.

Table 1, showing composition, reacting values, reaction, concentration, depth, and classification of waters from mines of sulphide ores.

	Mountain View		St. Lawrence		Green Mountain		Nettie		Dayton		Gilsonite		Anaconda		Capote		Capote		Capote		Capote		Capote		Burro Burro		Calloway		Calloway		East Tennessee		Deck Town		Deck Town		Victor		Alabama Coon		Shoal Creek		Holtschänburger		Holtschänburger		Holtschänburger		Holtschänburger		Waihi
	1 W.	A.V.	2 W.	A.V.	3 W.	A.V.	4 W.	A.V.	5 W.	A.V.	6 W.	A.V.	7 W.	A.V.	8 W.	A.V.	9 W.	A.V.	10 W.	A.V.	11 W.	A.V.	12 W.	A.V.	13 W.	A.V.	14 W.	A.V.	15 W.	A.V.	16 W.	A.V.	17 W.	A.V.	18 W.	A.V.	19 W.	A.V.	20 W.	A.V.	21 W.	A.V.	22 W.	A.V.	23 W.	A.V.	24 W.	A.V.	25 W.	A.V.	26 W.
SO_4	60.28	49.77	03.55	48.12	62.06	42.42	19.20	13.80	27.27	10.08	53.84	38.00	41.82	30.09	65.02	50.12	68.85	53.43	67.11	51.18	64.73	46.90	66.52	47.89	67.09	48.24	74.96	61.91	67.72	51.80	74.51	51.03	77.88	53.80	78.89	56.54	68.35	58.21	63.25	49.11	52.76	39.82	57.94	28.64	38.85	27.67	48.33	24.71	61.98	29.04	29.90
Cl	.02	.02	.31	.32	1.04	.96	4.20	4.16	38.72	32.08	11.70	11.37	5.42	5.31					.33	.34	.82	.81					.08	.09	.05	.05	.07	.07	.09	.08	.10	.10	.13	.13	.03	.03	8.00	9.61					5.88	4.08			5.01
CO_3					2.92	2.21	37.13	42.76						?																																							35.43
SiO_2	.06		1.13		3.54		15.93		1.36		2.88		16.58		.96		.71		.86		1.28		1.00		.58		4.46		5.92		2.38		2.81		2.96		.84		1.11		2.57		2.13		2.27		8.34		.63		6.33
NO_3																																																			
$BaCr$																																																			
H																									.03												.19														
Na	.04	.07	.94	1.49	2.47	3.51	8.60	2.93	3.81	4.87	17.49	20.22	5.10	7.71	undetermined		1.11	2.20	3.01	3.77	7.76	9.35	.70	.83	.23	.34	.64	1.11	.65	1.04	.18	.26	.44	.64	.44	.66	.47	.71	.57	.83	.67	1.06										7.28
K	.01	.01	.31	.29	1.03	.31	1.43	1.26	.52	.39	3.01	2.86	1.61	1.93											.20	.18	.33	.34	.26	.25	.24	.20	.41	.35	.46	.41	.12	.11	.01	.01	.40	.43									5.26
Li																																																		
NH_4																																																		
Mg	.14	.40	1.47	4.40	4.31	11.65	1.91	5.43	4.71	11.39	1.77	5.01	4.73	13.52	.77	2.44	1.45	4.45	1.31	3.91	1.64	4.71	2.69	7.76	.40	1.13	.64	2.09	.73	2.21	1.90	5.16	1.69	4.61	1.75	4.96	1.77	5.05	.26	.78	.11	2.12	3.96	7.73	4.41	8.19	6.88	13.90	3.90	7.11	.35
Ca	.26	.52	3.15	5.72	23.08	37.85	11.17	19.25	23.53	34.51	9.16	15.75	22.51	38.19	5.50	10.58	7.22	7.86	11.44	20.74	14.53	25.36	13.80	23.72	.67	1.15	2.38	4.71	3.60	6.60	7.19	11.86	2.71	4.49	2.60	4.47	3.97	16.38	3.55	6.61	11.32	20.57	19.08	22.85	21.33	30.83	26.02	27.00	27.05	29.90	14.05
Sr																											.02	.03	.01	.01	.01	.01	.13	.16	.04	.05			.02	.02	.42	.56	1.10	.95	.48	.40			1.41	1.17	
Mn	.01		.28	.37	.08	.10	.23	.09	.06	.08			1.15	1.40	2.98	4.18	2.05	3.60	2.32	3.07	1.69	2.15	2.24	2.81																																			
Al	.07	.31	1.39	8.02											undetermined		.78	3.22	.30	1.33	.73	2.82	.95	1.71	4.28	18.29	1.75	7.69	2.28	9.19	4.98	18.21	6.84	25.16	5.75	21.93	.43	1.65	1.46	6.03	.08	.32	.10	.26	.98	.95			.71	1.08	.66
Fe''			3.80	6.19																			1.20	2.22			2.45	5.22	6.61	13.01	5.63	10.01	4.61	8.23	4.23	7.95			4.88	8.16			1.68	2.15	1.21	1.47			1.41	1.68	
Fe'	.04	.06			.27	.32	.11	.14	.52	.02	.14	.11	.41	.51	3.85	5.31	14.11	18.86	7.95	10.35	3.47	4.34	7.42	9.15	2.50	26.46	8.61	12.23	10.56	13.90	.04	.05					5.19	6.46			.11	.14					3.13	2.75			.37
Cu	38.72	48.35	1.91	1.61							.03	.03			20.92	25.37	2.16	2.59	.91	1.04			1.39	1.51	3.08	3.33	3.39	4.23	1.30	1.50	1.23	1.28	1.77	1.85	1.84	2.00			.04	.05	.04	.05										
Zn	.35	.43	12.27	22.59	.05	.05					.18	.19	.87	2.3	undetermined		3.36	3.84	3.83	4.28	3.33	3.56	2.59	2.73	.38	2.08	.29	.35	.34	.38	1.64	1.66	.62	.63	.88	.93	12.64	13.30	24.79	28.31	22.31	24.78	12.61	9.17	4.86	3.36	4.22	3.17	.84	.57	
Cd			.97	.63																																	.09	.06	.10	.08										
Sn			.41	.25																																														
$Ni Co$			.01																																																
Pb																																																			
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	Mn, Cl		100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Traces	Ni, PO_4, Co, Li, As	PO_4, Ba, B, O_2, F	PO_4, Co, Li, As	Zn, Pb, C	PO_4, Cu, O_2		PO_4, Cu, O_2, Pb		PO_4, Ba, B, O_2, F		$PO_4, LiCl$														.61238		.8291		.8451		3.3102		.6794		.697		2.751		9.7175		.540		.37597		.38648		.2108		.33563		.0
Grames per Liter	117.848		4.2045		.655		.3501		2.1764		1.02		.2171		7.932		5.661		6.583		2.192		2.007		III acid		V acid		V acid		I acid		II acid		III acid?		V acid?		III acid		III acid?		III acid		III acid		III acid		III acid		III acid		
Reaction	III acid		III acid		III neutral		III neutral		III faintly alk		IV faint alkaline		Faintly alkaline		II acid		V acid		V acid		III neutral		Acer B		Acer B		A		A		A		A		A		A		A		A		A		A		A		A		A		A	
Class	A		A		B		B?		B		B		B		A		A		A		A		A		100'		90'		127'		180'		55' below surface		surface				A		B		A		A		A		A		A	
Depth	220'		1,200'		2,200'		300'		1800'						300'		pump		900'		400'		concentrator																													
Country Rock	Quartz Monzonite				Quartz Monzonite				Quartz		Monzonite		G. Monzonite		Quartz Diorite		Quartz Diorite		Quartz Diorite		Quartz Diorite		Quartz Diorite		Schists and		graywacke		Schists and		graywacke		schists and		graywacke		Limestone		Limestone		Limestone		Biotite schist		Biotite schist		Biotite schist		Biotite schist		Andesi

	Victor		Aloanna Coast		Snow Creek		Hoffstadtsberger		Hoffstadtsberger		Hoffstadtsberger		Hoffstadtsberger		Waihi-Tairua		Waihi-Tairua		Waihi-Tairua		Stanley		Nixon		Savage		Gould-Curry	
	19 W.	A.V.	20 W.	A.V.	21 W.	A.V.	22 W.	A.V.	23 W.	A.V.	24 W.	A.V.	25 W.	A.V.	26 W.	A.V.	27 W.	A.V.	28 W.	A.V.	29 W.	A.V.	30 W.	A.V.	31 W.	A.V.	32 W.	A.V.
	48.85	58.21	632.5	491.1	52.76	39.82	57.94	28.64	58.85	27.67	48.33	24.71	62.98	29.04	23.30	15.38	5.86	4.06	24.32	16.04	67.95	49.30	43.96	31.87	42.52	22.93	43.96	34.59
	.13	.13	.03	.03	.48	.48					5.88	4.08			5.71	1.62	7.30	6.83	5.31	4.15	.27	.27	4.18	4.70	.14	.10	.13	.14
					8.00	9.61									35.73	38.31	44.33	48.88	35.23	31.18			11.81	13.11	12.85	11.69	12.40	15.22
	.84		1.11		2.54		2.13		2.27		8.54		.63		6.33		10.57		7.24		1.45		8.71		3.41		9.60	
	.19						1.20	EB.28	1.21	27.13	1.06	24.39	1.34	29.45																
	.47	.71	.51	.83	.67	1.06									7.28	9.17	10.86	15.64	7.17	9.90	3.54	5.44	20.00	30.31	6.38	7.19	.07	.12
	.12	.11	.21	.21	.46	.45									5.26	4.45	7.08	6.80	4.20	3.42	2.33	2.11	.46	.41	.94	.62	15.78	15.30
	1.27	5.25	.20	.78	.11	2.12	8.86	7.13	4.41	8.19	6.88	13.91	3.00	7.11	.85	2.91	1.71	4.00	1.01	2.63	3.12	9.05	.85	2.43	1.21	36.67		
	3.47	16.33	3.55	6.61	11.32	20.50	18.28	22.85	27.33	39.83	22.02	27.00	27.05	29.90	14.05	21.56	11.63	12.12	14.24	22.52	6.24	10.99	9.25	16.08	16.58	21.40	18.35	34.63
			.02	.02	.42	.56	1.10	.95	.48	.40			1.41	1.17							5.18	6.66						
	.43	1.63	.14	6.03	.08	.32	.10	.28	.38	.95			.77	1.08	.66	2.25	.44	1.61	.89	3.12	.10	.39	.09	.35				
			4.88	8.16			1.68	2.45	1.21	1.47			1.41	1.68							5.49	6.42	.09	.19				
	5.19	6.45			.11	.14					3.13	2.75			.37	.49	.20	.24	.39	.49	.11	.14						
			.04	.05	.84	.05															2.57	2.85						
	12.58	13.30	24.79	24.31	22.31	24.78	12.61	9.17	4.86	3.36	4.22	3.17	.84	.57							1.65	1.78						
			.03	.06	.10	.06																						

The columns designated "W" show percentage of total solids, and the column following, designated by "R.V.", shows the same analysis with radicles calculated to reacting values.[a]

a. Palmer, Chase, Geochemical interpretation of water analyses: Bull. U. S. Geol. Survey No. 479, p.7.

The reacting value is the value obtained by dividing the percentage of a radicle by its equivalent weight. The valencies used are those of the oxides commonly assumed to be present in mine waters. The sum of the reacting values of all the positive ions should equal the sum of the reacting values of all the negative ions. Some analyses, however, when thus recalculated, will not balance. This is probably due to iron and aluminum oxides which are present to a greater or less extent as colloids and not as sulphates or other salts, and also to the failure on the part of the chemist to determine carbonates, hydroxides, and other radicles.

The reacting value enables one to determine the reaction of a water. Hydrolysis of a salt gives a solution which may be acid, neutral, or alkaline in reaction, de-

pending upon the relative strength of the acids and bases which reacted to form the salt. Salts which are not hydrolized give neutral solutions. Therefore (I)[a] those waters in which the strong acids (SO_4, Cl) are less than the alkalies are alkaline; (II) those waters in which strong acids are equal to the alkalies are neutral; (III) those waters in which strong acids are greater than the alkalies, but less than the sum of alkalies, earths, and metals, may be either neutral or acid, depending upon relative abundance of salts; and (IV, V) those waters in which strong acids are equal to or greater than the alkalies, earths, and metals, are acid in reaction. The reaction is stated beneath each analysis. When the 50 analyses are recalculated in accordance with the above considerations, 22 are acid, 14 are neutral, and 14 are alkaline. Results obtained by these recalculations do not always agree with the reactions stated by the chemist.

a. Numbers refer to Chase Palmer's classes.

Classes of Mine Waters.

A study of the chemical composition, concentration, reaction, environment, associated rocks, and temperatures of the waters in Table I shows five classes of mine waters.

Class A. The waters of this class are all acid in reaction. While a few contain free H_2SO_4, the reaction of most of the waters is due to the hydrolization of the salts of H_2SO_4 and, to a very small extent, to the salts of HCl. Salts of other acids are present only in traces. The salts of iron, copper, and zinc are the only salts present in large amounts whose hydrolysis will produce an acid solution. Of these, the salts of iron are present in all, the salts of zinc are found in only 19, and of copper in 15.

The compounds making up the bulk of the solids of Class A waters are mainly sulphates of calcium and of the heavy metals. Sulphates and chlorides of magnesium, sodium, and potassium are generally present in small amounts. Carbonates are not present in these acid solutions. Aluminum is present in large percentages in all, and manganese is generally present in large amounts. The

percentage of colloidal silica is generally low. The concentration averages 2.96 grams per liter, when the Mountain View and Central Tunnel waters are excepted. This concentration is higher than in any of the subsequent classes.

The following are waters typical of this class: Mountain View (1), and St. Lawrence (2), from Butte, Montana; Capote, (8), (9), (10), Central Tunnel (36), Stanley (29), Burra Burra (13), and Callaway (14), (15), at Ducktown; Victor (19), Alabama Coon (20), near Joplin, Mo.; Rothschönberger Stolln (22), (23), (24), (25) at Freiberg, Germany; and probably also Shoal Creek (21), Capote (11), (12) and Ruth (37).

These waters are the carriers in the processes of sulphide enrichment. All occur in deposits rich in sulphides, particularly in either pyrite, or pyrrhotite or marcasite, and probably all were collected in the zone of oxidation or not far below ground water level.

Class B. Generally the waters of this class are neutral, but a few are faintly alkaline, or faintly acid. Calcium sulphate is the dominant salt. It is probably

formed by reaction between calcite and H_2SO_4, $CuSO_4$, or other metallic sulphates. Sulphates, chlorides, and carbonates of magnesium and sodium are present in all, with a less amount of potassium sulphates. Salts of aluminum are present in small quantities. Traces or small percentages of copper, zinc, lithium, arsenic, lead, and phosphorous are often present. Colloidal silica is relatively larger than in Class A. The concentration is variable. Waters illustrating this class are: Green Mountain (3), Brook's Porphyry (38), and Homestake (42). The inferences are that these waters were collected either below ground water level or at great depths.

There are two variations of Class B. One shows a large increase in NaCl. This is particularly illustrated by several waters from Butte, viz., Gagnon (5), Glengarry (6), and Anaconda (7). It does not seem probable that the high chlorine content is due to aridity nor to the leaching of the surrounding rock, nor yet to the excreta of men and horses, because other Butte waters, probably formed similarly except as to depth, show a low NaCl content. The source of the NaCl is doubtful; perhaps it is

a contamination by a foreign water from a deep source.

A second group contains $CaCO_3$ in appreciable amounts. Calcium carbonate is soluble only in waters containing CO_2, a fact which indicates that these waters are not associated with iron sulphides under conditions which would produce acidity. The Solomon (40) and Homestake (41) belong here, as do probably the waters of Shoal Creek (21), Nettie (4), and Waihi-Tairua (26), (28).

Class C. These waters closely resemble the vadose waters from regions of little or no sulphides. In the waters of this class collected near the surface $CaCO_3$ is plentiful. If collected at depths, and particularly if associated with buried salt beds, NaCl is abundant. In either case sulphates, carbonates, and chlorides of sodium, magnesium, manganese, aluminum, and iron are present. Colloidal silica is relatively high. The concentration is low and the reaction of all these waters is alkaline. The Federal Loan (44), Black Prince (45), Victoria Reef (46) are examples of this class.

Class D. These waters are all alkaline, ascending, and warm or hot. They are associated with recent igneous rocks. Borates or carbonates of sodium are the principal salts. Calcium and magnesium salts and silica are present in small amounts. Hydrogen sulphide is often present. Other elements frequently present are fluorine, nitrogen, and strontium. The concentration is variable. This class has been discussed at length by Emmons and Harrington.[a] The waters of Sulphur Bank(49), (50), and Geyser (47) belong to this class.

Class E.[b] These waters are neutral or alkaline. They are chiefly solutions of sulphates and carbonates of sodium, potassium, and calcium. Magnesium salts are usually present. Salts of manganese, aluminum, and iron are often present. The percentage of silica is high. The concentration is not above one gram per liter. These waters combine the chemical characters of Class D with those of preceding classes. They are often associated with thermal springs in regions of recent igneous rock. The composition suggests the possibility that these waters

a. Emmons, W. H., and Harrington, G. L., Econ. Geol., vol. 8, 1913, p. 653.
b. Lindgren, W., Mineral deposits, p.42.

are mixtures of descending vadose waters with ascending thermal alkaline waters. The Savage (31), Bachelor (39), Gould and Curry (32), (33), Hale and Norcross (34), and probably Homestake (43), and Waihi-Tairua (27), belong to this class. All these are found in regions of late Tertiary vulcanism, although one, from the Homestake, was found in pre-Cambrian rocks. These pre-Cambrian rocks are cut by Tertiary intrusives.

In general these classes express the work done by each water. Class A is the transporting agent in processes of sulphide enrichment. Class B results from Class A when waters of Class A have been depleted of their metallic salts. Class C is the type of water occurring in sulphide mines which does not accomplish any enrichment. Class D, mingling with the waters of Class A, produces waters of Class E, in consequence of which the salts of the metals are precipitated.

Observations on Table I.

Inspection of Table I reveals several interesting facts. We may first consider zinc and copper. Of the three acid solutions in which zinc is absent (26, 36, 37), one is practically neutral, and two are from deposits nearly free of zinc minerals. The acid waters lacking copper (19, 22, 23, 24, 25, 26, 37), are from mines nearly free of copper ores, or in which copper is very subordinate. Because of the high concentration of the sulphate radicle in acid solutions, most of the copper is present as $CuSO_4$.

Gold and silver are found in traces in the Central Tunnel and C. and C. waters of the Comstock Lode. Both contain ferric iron, probably as ferric chloride, since both solutions contain the chlorine radicle in abundance. One of these solutions is acid and the other is neutral. The acid solution contains no manganese despite the fact that the ores are highly manganiferous.

The lead radicle is found only in carbonate waters of alkaline reaction, doubtless it is present as $PbCO_3$.

The concentration of aluminum salts decreases decidedly with decreasing acidity. When aluminum is present the sulphate radicle is high, indicating that the salt is usually present as $Al_2(SO_4)_3$, although small amounts may be present as the colloidal hydroxide. Since the affinity constants for iron, copper, and zinc are higher than for aluminum, any free H_2SO_4 in the water would first form sulphates of the heavy metals before forming aluminum sulphate. Only if an excess of acid was present over that necessary to combine with metals would the feldspars, sericite, etc., be rapidly attacked to form $Al_2(SO_4)_3$. That this is often the case is shown by the association of the Comstock, Waihi-Tairua, Capote, and Tonopah waters, with large amounts of kaolinitic material.

In all neutral or alkaline solutions, when manganese is present, the iron is in the ferric form. Ferric iron is found in several of these neutral or alkaline solutions, undoubtedly as a hydroxide.

Cadmium salts occur in two acid waters which contain zinc. Cadmium, tin, nickel, and cobalt occur in small amounts and only in acid solutions.

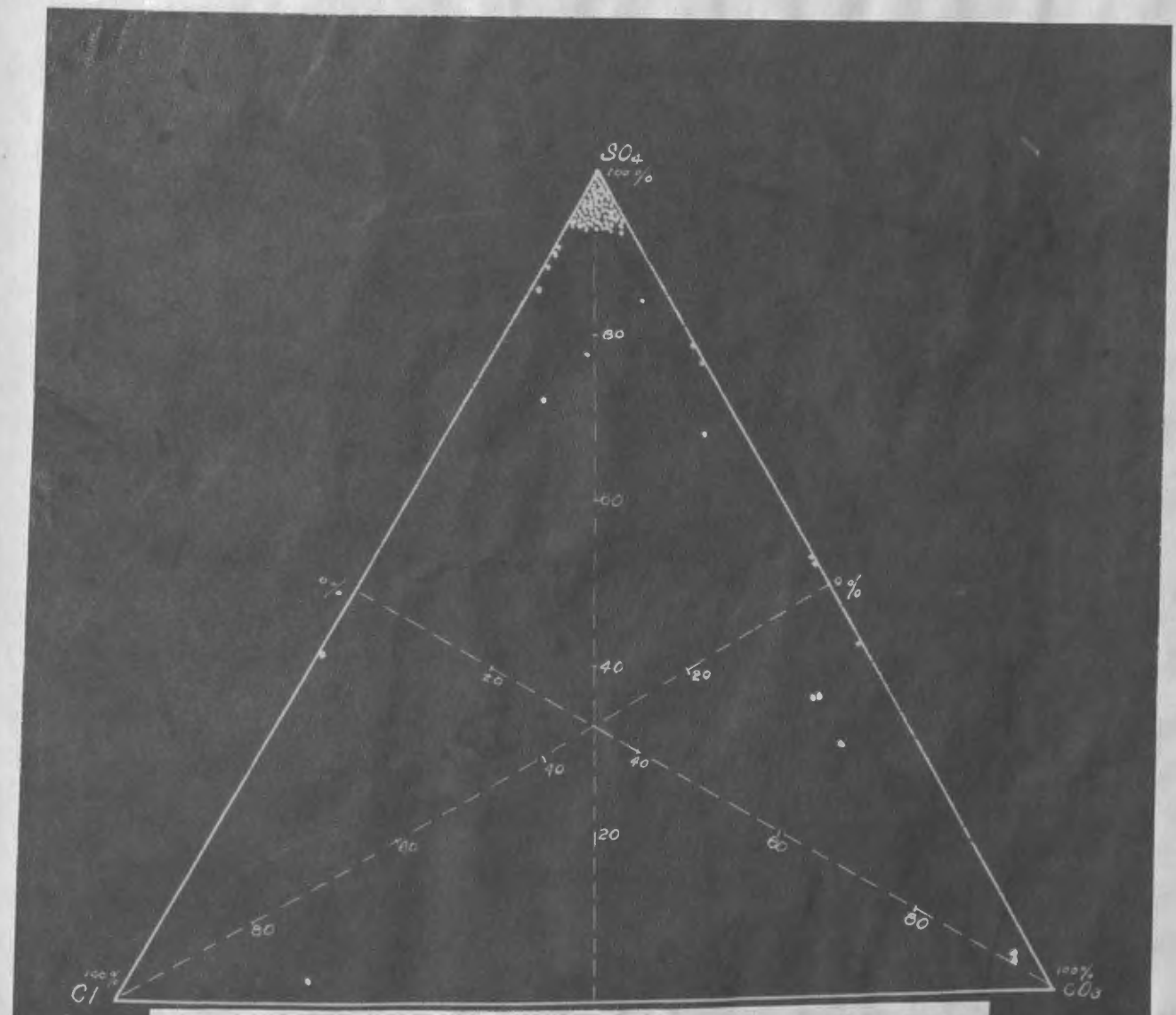

Fig. 1. Diagram showing relative abundance of SO_4, Cl, and CO_3.

The relative abundance of the sulphate, chloride, and carbonate radicles in these waters is shown in figure 1. Sulphates are low and carbonates and chlorides correspondingly high in waters high in sodium, potassium, calcium, and magnesium. Silica is always present in colloidal form.

Some of these waters contain free H_2SO_4, which will react with many sulphides to generate H_2S. Alkaline sulphides are found in some ascending thermal waters of Class D. When such waters as these mix with vadose acid waters to produce waters of Class E, the sulphates of the heavy metals will be precipitated.[a] Many of the waters show an increase in calcium and magnesium sulphate accompanying the decrease in the salts of the heavy metals. This indicates that in some cases the acid waters react with carbonate minerals. Reactions like the following undoubtedly take place, where carbonates are present, between most descending acid solutions and the wall rock.

$$2CuSO_4 + 2CaCO_3 + H_2O = Cu(OH)_2CO_3 + CaSO_4$$

$$ZnSO_4 + CaCO_3 = ZnCO_3 + CaSO_4$$

a. Grout, F. F., Behavior of cold acid sulphate solutions: Econ. Geol., vol. 8, 1913, No.5.

State of Oxidation of Mine Waters.

The waters collected are in an abnormal state of oxidation due to mining operations. In the Ruth mine, where the water level has been reduced 300 feet in a few years, the oxidation of the ores has raised the temperature several degrees. At the Burra Burra the waters collected as they emerged from the wall rock have only ferrous iron, while those waters standing in the Callaway shaft have both ferrous and ferric iron. The waters of the Green Mountain mine at Butte, collected a day after a crosscut was opened, contain only ferrous iron. It is, therefore, not probable that ferric salts are present except in very small amounts in normal mine waters below the vadose zone. Since H_2S oxidizes so easily and disappears from mine waters so rapidly, the salts of iron are the only compounds which form a ready indicator of the state of oxidation of a mine water.

	Fe	Zn	Cu	Al	Mn	Na	K	Mg	Ca	SO_4	
Average percent in all acid waters	6.0	5.6	3.8	1.7	0.7	1.0	0.7	2.0	8.9	2.6	22 acid waters with total solids averaging 2.98 grams per liter
" " in waters where present	6.2	6.5	5.3	1.9	1.1	1.2	1.0	2.0	8.9	2.6	
Number of waters in which present	21	19	15	20	16	18	16	22	22	22	
Average percent in all neutral waters	1.3	0.5	0.1	0.2	0.4	5.7	3.6	3.3	15.7	6.3	14 neutral waters with total solids averaging .82 grams per liter
" " in waters where present	1.8	2.0	1.4	0.4	1.0	5.7	3.6	4.1	15.7	6.3	
Number of waters in which "	10	3	1[a]	6	5	14	14	11	14	14	
Average percent in all alkaline waters	0.2	0.1	0.0	0.1	0.2	11.2	6.1	2.3	12.6	8.6	11 alkaline waters with [b] total solids averaging .66 grams per liter
" " in waters where present	0.2	0.4	0.0	0.2	0.4	11.2	6.7	2.5	12.6	8.6	
Number of waters in which present	10	3	1[a]	6	6	11	10	10	11	11	

a doubtfull reaction b Class D waters omitted

Table 2. showing percentage of radicles in waters of different reaction

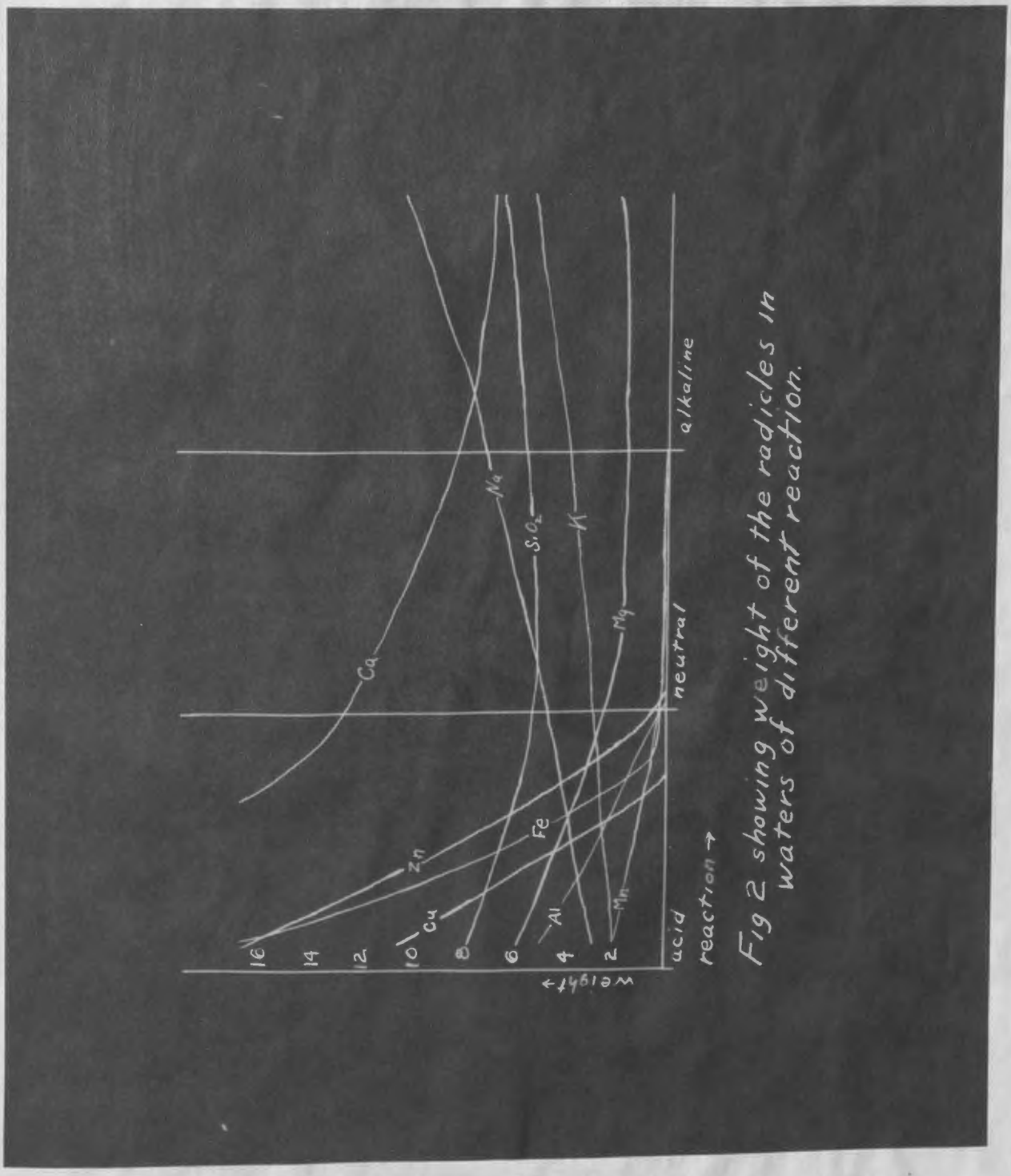

Fig 2 showing weight of the radicles in waters of different reaction.

Changes with Acidity and Depth.

The average total concentration of acid solutions is 2.96 grams per liter, of neutral solutions the concentration is .82 grams per liter, of alkaline solutions it is .66 grams per liter. In these averages the Mountain View (1), at Butte, and Central Tunnel (36), at the Comstock Lode, have been omitted. All mine waters are far from being saturated solutions; the average is about one hundredth normal.

If the percentages shown in Table II are multiplied by the average total concentrations, the curves shown in figure 2 are obtained. These curves show that the actual concentration of any salts, excepting those of sodium and potassium, decreases as the solution changes from acid to neutral and from neutral to alkaline. Since salts of the heavy metals and of aluminum and manganese occur in large amounts in acid solutions, in small amounts in neutral, and are practically absent in alkaline solutions, they may, within certain limits, be used as indices of the reactions of the solutions in which they occur.

Probably all the acid waters of Class A were collected relatively near the surface, while the neutral or alkaline classes of waters from mines of sulphide ore deposits were found in the main at great depths. In some mines a decrease in acidity is shown by waters collected at successive depths. For instance the Capote waters of the 300-foot level contain free H_2SO_4. At the Capote 900-foot level the waters contain no free acid. At Butte the Mountain View (1) and St. Lawrence (2) waters are acid, while the deeper waters of Gagnon (5), Glengarry (6), and Anaconda (7), are neutral or alkaline. At Homestake the two shallow waters are neutral and the deeper water is alkaline. All the very deep waters are neutral or alkaline, a fact which is illustrated by the Homestake 1100 and 1550-foot level water, the Green Mountain 2200-foot level, Victoria Reef 4280-foot level, and Gagnon 1800-foot level.

As waters descend in depth the concentration of salts of heavy metals decreases. At Capote the 300-foot level has 20 per cent of the total salts in solution as sulphates of the heavy metals and at the 900-foot level only

12 per cent are still present. At Ducktown the Burra Burra, at 100 feet, has 26 per cent; the Callaway, at 127 feet, has 12 per cent of heavy metallic sulphates. This same decrease is shown by the waters in the Ducktown mine at Ducktown, and by the waters at Butte. In general, aluminum salts decrease with depth. For instance, the Burra Burra water collected above ground water level has 4.3 per cent of $Al_2(SO_4)_3$, and the Callaway at 127 feet has 2.26 per cent of aluminum salts. On the other hand the alkalies increase with depth. Since the upper waters are acid and the deeper waters are neutral or alkaline, then the concentration of all the salts excepting those of sodium and potassium decrease with depth, a fact which is brought out by figure 2.

The change in the composition of the waters is also related to zones. At Capote the chalcocite zone ceases at the 900-foot level, as do also the copper salts in these deep waters. In the same mine the relative abundance of zinc salts increases below the chalcocite zone, showing that zinc salts are carried to much greater depths and are not precipitated so readily as the copper salts.

At Ducktown the chalcocite zone is 100 feet below the surface and below this level the waters show a decided decrease in copper salts. The enriched zone at Waihi-Tairua is at about 500-600 feet, and the waters collected below this level are free of copper salts.

In the Ducktown waters the total concentration decreases with depth. At Homestake the concentration increasss downward to the 1100-foot level and then begins to decrease, losing nearly half of its dissolved material in 500 feet. At Waihi-Tairua the deepest waters have the lowest concentration. If acidity decreases with depth in all mine waters, and if concentration decreases with acidity, then the concentration must decrease with depth.

If descending meteoric waters, as far as they have been observed, become less and less concentrated with metallic salts at depth, is it rational to assume that deep waters are agents of the formation of primary ore deposits under conditions that come under human observation?